Changes in the Wave-Frequencies of the Lines of Emission Spectra of Elements, their Dependence upon the Elements themselves and upon the Physical Conditions under which they are Produced.

Dissertation

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by

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Preliminary Remarks.

It is well known to spectroscopists that the character of the emission spectrum of an element depends greatly upon the physical conditions under which it is produced. If the element be in the solid or liquid state its spectrum is a continuous one, and discontinuous when it is in the form of an attenuated gas. The discontinuous spectrum may consist either of bands or of isolated lines or of both, according in part to the substance used and in part to the conditions under which the spectrum is formed. In general the number of lines that can be

detected and their intensities increase with increase of temperature, though the intensities of certain lines seem to reach maxima and then to decrease as the temperature is raised. Increase in the density of a gas or vapor increases the width of its spectral lines. Some lines spread out symmetrically, others unsymmetrically. In the latter case the chief increase in width is usually towards the less refrangible or red end of the spectrum. A somewhat similar increase in the width of lines, together with certain polarization phenomena may be produced, according to Zeeman,[1] by placing the gas in a magnetic field.

1. On the Influence of Magnetization on the Nature of the Light Emitted by a Substance — Phil. Mag. March '97.

Again, whether a line is reversed or not depends in part at least upon the thickness of the absorbing layer. Under proper conditions, especially as to quantity of material, certain lines may give a double or even a multiple reversal. Finally a single element, as argon for instance, may give one or another of two distinct line spectra owing to the character of the electric discharge used to produce it, and to the pressure of the gas.

Not only emission but absorption spectra also are known to be subject to changes. One of the most important of these changes was observed and described by Kundt, who says that the position of an absorption band depends upon the substance in which it is dissolved or incorporated. This

that the band is displaced towards the red end of the spectrum when the substance producing it is dissolved in a strongly dispersive medium; or, to use his own words, as they occur in an article[1] on absorption spectra. "Hat ein farbloses Lösungsmittel ein beträchtlich grösseres Brechungs- und Dispersionsvermögen als ein anderes, so liegen die Absorptionsstreifen einer in den Medien gelösten Substanz bei Anwendung des ersten Mittels dem rothen Ende des Spectrums näher als bei Benutzung des zweiten".

In view of the reciprocal relation between absorption and emission of radiations, it would seem that one might

1 Ueber den Einfluss des Lösungsmittels auf die Absorptionsspectra gelöster absorbirender Medien. Wied. Ann.

suggest the possibility of a similar phenomenon, that is shift of lines, in the case of emission spectra. Indeed some writers have reported shifts of certain spectral lines, and besides something of the kind is suggested by the theories of both Lommel[1] and Wüllner[2]. However these observations were all but certainly illusion, as others have asserted, and as will be explained further on, and the theories are at least incomplete since they do not agree in all respects with observations. In considering them I shall confine myself to those parts that deal with the displacements or

1. Theorie der Absorption und Fluorescenz, Wied. Ann. 3 p. 251.
2. Ueber allmähliche Ueberführung des Bandenspectrums des Stickstoffs in ein Linienspectrum Wied. Ann. 8 s. 590

shifts of the lines.

According to Lommel's[1] theory the spectral lines increase in width, chiefly on the red side, and shift in the same direction when the density of the gas producing them is increased. He says: "Bei vergrösserung der Dichte oder des Drucks eines Gases erleidet die hellere Spectrallinie eine Verbreiterung und gleichzeitige Verschiebung nach der weniger brechbaren Seite hin."

This theory makes the spreading of a line and its displacement depend upon the same thing—namely, the increase of the density of the gas whose lines are affected. According to it the spreading must always be chiefly

1 Theorie der Absorption und Fluorescenz, Wiedemann 3, p. 251

towards the red end of the spectrum, and the lines must shift only when they are spread out; in fact the shift of a line is due, in terms of the theory, to the unsymmetrical broadening and to nothing else.

As a matter of fact, while many lines are spread out by increase of the density of the gas producing them, chiefly towards the red end of the spectrum; many others are broadened symmetrically, and others even spread out chiefly towards the more refrangible or violet end. Therefore by merely increasing the density of the luminous gas or vapor, without change of total pressure, the centers of certain lines are moved towards the red and others towards the violet of the spectrum; while

those lines that spread symmetrically are not displaced at all. Besides the reversals, which of course give the positions of the lines, are never displaced in the slightest by any increase in the density of the luminous gas or vapor, so long as the absolute pressure is kept the same.

The shift discussed in this paper probably does not depend in the least, as will appear from the experimental results, upon the density of the gas or vapor producing the lines, but only upon the absolute pressure; and apparently it has no connection with the broadening, either symmetrical or unsymmetrical, of the lines themselves. It would therefore appear that Lommel's theory, though ingenious and well worked out, is no

wise predicts the observations described in the following pages.

In support of that part of his theory which demands a shift of the lines, Lommel refers to the experiments of F. Zöllner[1] and J. J. Müller[2], both of whom used the common method of putting a bead of salt in a Bunsen flame and then examining by suitable methods the light so produced. The intensity of the flame and the quantity of salt in it were both varied, and some of the results they obtained indicated a

1. Ueber den Einfluss der Dichtigkeit und Temperatur auf die Spectra glühender Gase. Pogg. Ann. CXLII. 88

2. Beobachtungen über die Interferenz des Lichtes bei grossen Gangunterschieden. Pogg. Ann. CL. 311.

movement of the lines towards the red end of the spectrum. This can be explained by, and was almost certainly due to, unsymmetrical spreading of the lines examined. Certainly neither observer found (the conditions were not such as would produce it) a true displacement of the lines in the sense that the term is used in this paper. That is they did not find a given line, as produced under various conditions, differing in no wise other than in mere position in the spectrum; nor do they speak of the displacement of the reversals.

The other theory referred to, that of Wüllner, assumes all variations in the spectrum of a substance to be due to what might be termed external

changes, such as temperature, density and the like, and in no case, not even in the change from band to isolated line spectra, to any alteration of molecular grouping. Wüllner assumes the correctness of Zöllner's equation,

$$E = \{1 - (1-\alpha)^{d\delta}\}\varepsilon ,$$

in which E is the total amount of light of a given wavelength, d the thickness, δ the density, and α the coefficient of absorption of the luminous gas or vapor, and ε the power of a perfectly black body, at the same temperature as the luminous gas, to give out light of the given wavelength. Now if α is a function not only of wave length, but of temperature too, and such a function of them that its maximum value

occurs at different places for different temperatures, as Wüllner assumes it to be, of course a line may be shifted by merely changing the temperature of its source. Besides, the shift may be in either direction, and may be either regular or irregular. In fact if α is such a function of temperature and of wavelength, as that just described, one can only say that a given change in temperature will produce a greater or less change, in one direction or the other, in the position of a line in the spectrum. In certain respects the conclusions of this theory are not well supported by careful observations, and for this reason it is not now, if ever, much received by spectroscopists. In regard to the displacements of the lines it is stated

by Kayser[1], in an article in which he discusses the above theory quite fully, that he knows of only one line, the sodium line D_2, of which accurate measurements have indicated a shift, and that in this case the shift is illusive, and due to unsymmetrical broadening. His words are: "Mir ist nur ein Fall bekannt, wo man nach genauen Messungen eine Verschiebung geglaubt beobachten zu können: nämlich bei der Linie D_2; aber dies ist, wie an anderer Stelle gezeigt werden soll, eine Täuschung: D_2 verbreitet sich nicht gleichmässig nach beiden Seiten, daher

1 Ueber den Ursprung des Banden- und Linienspectrums. Wied. Ann. 42. p. 310.

scheint sich die Mitte etwas zu verschieben, aber der meiste Theil, die eigentliche Linie bleibt genau an ihrer Stelle". In another place, Kayser says that neither lines nor bands have ever been observed to shift. "Eine Verschiebung von Linien ist selbst bei den genauesten Messungen niemals beobachtet worden, weder beim Banden- noch beim Linienspectrum".[1]

Before the present work was begun, no accurate measurements, so far as I can learn, had shown a true shift independent of all other changes, of the spectral lines, nor had it been demanded by theory. Lommel's theory made the shifts of the lines a consequence of their unsymmetrical spreading,

1. Winkelmann, Handbuch der Physik II. 1, p 425.

while Wilting's theory, though capable of explaining any one of [illegible] phenomena in the spectra [illegible] to predict shifts of lines at all definitely. It only states what is perfectly evident in this particular: namely, that by changing the conditions under which the spectrum of a substance is produced its lines may or may not be displaced, that is their displacements will be either zero or else plus or minus a greater or less amount, which of course is really predicting nothing as to shifts, except that they are possible.

As stated above neither of these theories has been supported as to the shifts of the lines, by observations. Instead then of regarding the wave-frequency of a line as being but a thing or

another, owing to circumstances, practically all spectroscopists have considered it a constant of reference, subject to no possible change. All observers who have given us tables of accurately determined wave-lengths have, at least tacitly, made this assumption, and upon it are based the estimates of the velocities in the line of sight of many of the fixed stars. The same assumption is made in comparing solar and stellar with terrestrial spectra for the purpose of determining the constituents of the sun and stars, and when coincidence of lines, evidently the same, was not exact, the discrepancy was naturally referred to disturbances of the apparatus during the process of photographing.

This assumption of the constancy

of the wave-frequency has led to the hope, a vain one it seems, that the wave-lengths in vacuo or in any given medium, of spectral lines may serve as ideal units of reference, that is units whose values are absolutely the same at all times and under all circumstances.

While the wave-frequencies of spectral lines depend, as shown further on in this paper, upon the physical conditions under which they are produced and therefore their wave-lengths are not ideal units of reference, still it is easy to obtain spectral lines, as often as desired, under conditions so similar, that their wave-lengths are more nearly ideal length units than those which at present

we can obtain in any other way; consequently the results of experiments described in the following pages do not materially affect (though they show precautions that must be taken) the value of Professor Michelson's[1] most ingenious and careful determination of the wave-lengths of the red, green and blue lines of the spark-spectrum of cadmium vapor at low pressure, in terms of the standard meter.

Object of the investigation.

The work described in this paper was suggested by Dr. Ames

1 Détermination expérimentale de la valeur du mètre en longueurs d'onde lumineuse.

and begun for the purpose of examining minutely the effect of pressure on the arc spectra of various elements, and in particular for noting the effect if any on the wave-lengths of the lines. The idea of examining arc spectra under pressure occurred to Professor Rowland several years ago and the apparatus used in the present investigation is that which he had constructed for this purpose. Constant work however, along other lines prevented him from making any observations with it.

The first accurate observations, to the best of my knowledge, that suggested the possibility of a functional relation between the wave-frequencies of spectral lines and the conditions under which the lines are produced were

made by Mr. L. E. Jewell in the physical laboratory of the Johns Hopkins University. The suggestion came in part from the fact that Mr. Jewell's numerous and careful measurements of the same lines in the arc and solar spectra showed a want of coincidence which varied for different elements. While this want of coincidence was never great, it nevertheless appeared too regular to admit of the seemingly obvious explanation that it was not due to any real difference in wave-length, but to some displacement of the apparatus during the exposure of the photographic plates.

Mr. Jewell had also obtained slight real or apparent displacements of certain lines by changing the amount of material in the arc. It was this chiefly that led Dr. Ames to suggest the present investigation.

The only way, of course, to determine whether such a functional relation between wave-lengths of spectral lines and the conditions under which the spectra

are produced actually exists, was by direct experiment, and it therefore seemed advisable to examine arc spectra under different conditions, especially of pressure and if possible of temperature too since the conditions under which solar and ordinary spectra are produced may differ greatly in both these respects.

Another reason for taking up this investigation was found in the fact that the wave-lengths of the red, blue and green cadmium lines, as determined by Professor Michelson for the purpose of accurately comparing them with the standard meter, were less in each case than those of the same lines as determined by Professor Rowland. The differences are ·2[illegible] of an Angstrom unit for the red, ·173 for the green and ·186

for the blue line. This difference amounts to only about one part of the wave-length in thirty thousand, and in itself is not very surprising since the methods followed by these two observers were totally different, but it is rather surprising that these differences are not constant. Since quite differences of physical conditions under which the spectra were produced (Michelson worked with spark spectra at low pressure while Rowland used the arc at atmospheric pressure) suggest a possible explanation of the want of agreement in their measurements. The results of numerous examinations of various spectra as produced under different pressures do account for a part, though only about five percent of the above differences, but fail to account why the differences should not be the same for all the lines.

Apparatus used.

The grating used in all this work was a six inch Rowland concave of fifteen and a half feet focal length and ruled with 20,000 lines to the inch. It was mounted in the usual way, as fully described by Dr. Ames in the Johns Hopkins Circular of May, 1881. The arc was produced by a direct 110-volt current of any amperage desired; and it was found necessary to make the strength of the current very different for different substances and also for different amounts in the arc of the same substance. At times the current was small - only a few amperes - while it occasionally, judging from the fuses blown, was not less than fifty.

The effect of varying the strength of the current will be discussed further on. The poles were used vertical and parallel to the slit of the spectroscope. Horizontally mounted poles were also tested, and the results will be given in the proper place, but it did not appear necessary to use any other than the vertical mounting which was found to be much the more convenient of the two tried.

A few photographs were taken, while working on the spectrum of iron, with one carbon and one, the lower, iron pole. Zinc, brass, copper and other metal poles have also been used. In all other cases both poles were of carbon, and the lower one was bored axially to a depth of from one to three inches. This cavity, which was about an eighth of an inch in diameter, was filled with the substance or substances whose spectrum was desired. Very

often elements were used in the metallic form, but as a rule it was more convenient and occasionally, as in the case of sodium and potassium, even better to use some compound. The quantity of the element in the arc could easily be decreased, as was often done, by mixing the element or compound used to a greater or less extent with carbon dust or for charging the pole with it. In nearly all cases the pole carrying the charge was made the positive one.

The pressure around the arc was obtained in every instance by pumping air into the apparatus designed for this work by Professor Rowland, as stated above and used by Messrs Duncan, Rowland and Todd in their examination of the

electric arc under pressure[1]. The structure of this apparatus may be understood by aid of the accompanying sketch, See Plate I. in which A is an iron cylinder fourteen inches high and seven inches in diameter. B, B are suitably constructed stuffing boxes through which the rods C, C pass practically air tight. These rods are insulated from the smaller rods H, H which they contain and which carry the carbons. N is the negative and P the positive pole as commonly used. The latter is represented partly in section to show the cavity S in which the substance whose spectrum is desired is placed. The carbon N can be raised

1. Electrical World, 22, 1893.

and lowered by means of the rack R and pinion G, and the carbon P can be brought to the proper position with the nuts and screws D, D' and L, L. The light reaches the slit of the spectroscope by passing through the side tube T, which is closed at Q with a plane quartz disc. The object of using quartz instead of glass is of course to avoid as far as possible the absorption of the ultra violet light. The air is pumped in through the tube U which can be opened and closed by means of the stopcock b, and the pressure is given by a Bourdon gauge E, reading from one to twenty atmospheres.

Method of Photographing.

For the purpose of accurate comparison it was necessary to obtain side by side photographs of the spectra of the substance in question as given by the arc under the two pressures used, the lowest of which was always that of one atmosphere. It was also necessary to guard, as far as possible, against any accidental movement of the camera or other part of the apparatus during the exposure and to be able to surely detect any such accidental disturbance should it occur, since any slight movement of the apparatus during, and especially between successive exposures on the same plate, would necessarily lead to false results.

The first of these requirements, that is the obtaining of the spectra in such way that they could be accurately compared was met in the same manner (and with the same apparatus) that Professor Rowland met a similar requirement in the comparison of solar and arc spectra, that is by providing the camera, which takes a nineteen by one and a quarter-inch plate, with a rotating shutter so constructed that in one position it shields the sides along the entire plate and leaves a narrow middle strip exposed, while in a certain other position it shields the middle strip and exposes the sides. In nearly every case the middle strip was exposed to the arc under pressure; after which the air was let out from the cylinder, the shutter adjusted and the

sides of the plate exposed to the arc at atmospheric pressure.

The method used at first for detecting accidental disturbances was as follows. By means of an auxiliary shutter a small portion of the middle strip was first exposed to the solar spectrum, all other parts of the plate being shielded, then the remainder of this strip to the arc under pressure, then the corresponding sides to the arc at atmospheric pressure, and finally the remaining portions to the solar spectrum. This process secured a short section of solar spectrum, the middle portion of which was exposed before and the sides after the exposures to the arc. Consequently any disturbance of the apparatus between the first and last exposures was made evident by breaks in the solar lines.

It soon became evident however that this method, though accurate, was not necessary, since the lines of the carbon bands, some of which occur on nearly every plate, are never measurably displaced and therefore serve perfectly to detect any disturbance of camera or other part of the apparatus during or between the exposures.

<u>Method of measuring.</u>

The shifts of a few lines were determined by direct observations with a micrometer eye-piece, but practically all measurements were carefully made on the photographs with a most accurate dividing engine, especially constructed by Professor Rowland for this sort of work, and used in determining

Rowland's[1] table of standard wave-lengths. The dividing engine and the micrometer eyepiece are both constructed to read directly to hundredths of a millimeter, and may be estimated to thousandths of a millimeter.

Most of the plates were taken in the second spectrum when the dispersion is a little more than one millimeter per Ångström unit, though a few were taken in the first when the dispersion is one half that of the second, and many were taken in the third when it is three halfs that of the second. In all several hundred negatives were measured and the shifts determined of those lines whose positions are well defined by reason either of their sharpness or of their reversals.

[1] A. and A., 12, 1893.

To facilitate the measuring of the shifts without decreasing the accuracy a system of double cross-hairs was placed, as shown, see Plate II. in the field of the microscope. In the process of measuring, the microscope was kept fixed and the negative moved along by the micrometer screw until the cross A was on the center of a given line in the middle strip, that is a line produced by the arc under pressure, when a reading was taken. The plate was then moved forward by the screw until the crosses A, B were on the center of the same line as formed on the sides of the negative by the arc at atmospheric pressure, when another reading was taken, and so on for other lines. The plate was then reversed and the same process repeated.

Now let $\underline{s}$ be the shift of any line and $\underline{l}$ the difference in readings that would be given by the crosses A, and B, B when there is no shift, and let the direct reading of the crosses B, B be λ, and the reversed $\underline{d}$. By the direct reading I mean that which is obtained when the plate is being moved so that the successive lines to come into the field of the microscope are of increasing wave-length, and by "reversed reading" I mean that obtained when the plate is moving so that the successive lines seen through the microscope are of decreasing wave-length. The direct reading then as given by A will be $\lambda - \underline{l} \pm \underline{s}$, and the reversed $\underline{d} - \underline{l} \mp \underline{s}$. Evidently $\lambda + \underline{d}$ is a constant from which, if the reversed readings be subtracted, remainders will be obtained equal respectively to λ and

$\lambda + \underline{l} \pm \underline{s}$. Consequently the average of the two readings given by the crosswire is λ and that of those given by $+\lambda \pm \underline{s}$, their difference being the shift $\pm \underline{s}$. By this means the accuracy of the measurements is rendered very considerable. In the case of extra good lines the error should not exceed from two to three thousandths of an Ångström unit.

Experimental Results.

A little preliminary work was done with the arc spectra, at atmospheric pressure, of cadmium and a few other elements. The chief changes found were those of intensity and width of the lines, both of which increased with increase of material. A large amount

of material in the arc caused a reversal of many lines, but in every case examined the reversal coincided very closely, if not exactly with the position of the corresponding fine line as produced by a small amount of the substance.

The substance whose spectrum as formed under pressure was first examined was cadmium, and it was at once noticed that the positions of its lines were very appreciably changed by a pressure of one three or four atmospheres. Subsequently the lines of a large number of other substances were similarly examined, and in every case their positions, except those of lines of certain bands, were more or less changed.

That this change in position of the lines is not due to any strain or movement of some portion or other of the apparatus, may be shown in several

way, but it is easier and also best shown by the fact that on the same plate lines due to different substances are displaced to very different extents, whereas they should be equally displaced if the displacement was due to some disturbance of the apparatus while photographing. Nor is the observed shift due to unsymmetrical broadening, since in many cases equally fine and sharp lines were obtained at high and normal pressures, the only important difference of the lines as obtained under the two conditions being that of position. Not only were numerous lines of this character photographed, but the evidence as furnished by the negatives was also checked and confirmed by a number of eye observations, especially on the cadmium lines λ6438.680 and λ 5086.001, and the sodium lines

D_1 and D_2. By filling the positive pole with fused potassium sulphate, which usually, like the specimen used, contains more or less sodium, it was easy, at any pressure, up to ten or more atmospheres, to get the sodium lines D_1 and D_2 and to retain them some minutes as beautifully fine and sharply reversed lines; differing in no respect from the same lines as obtained at a very different pressure except quite decidedly in position. A further reason for the statement that the shift is not due to unsymmetrical broadening of the lines is found in the fact that the wave lengths of all fine and sharp lines, and also of the reversals of heavy ones, increase with increase of pressure around the arc, no matter how the

lines may spread out, symmetrically or chiefly towards either side. A splendid example of this is furnished by the pair of sodium lines λ 3302.504 and λ 3303.119. These lines are quite unsymmetrical, and spread chiefly towards the violet or more refrangible end of the spectrum, but their reversals are greatly shifted in the opposite direction. Neither is the observed shift due to the disappearance of one line and the appearance of another of slightly different wave length, because the wave length of a line increases regularly instead of by jumps as the pressure is increased, and besides it is not difficult to observe, while the pressure is being let off, either a fine line or the reversal of a heavy one gradually change its position without alteration in width

or any other respect. This last experiment requires a little care, since a too sudden drop in the pressure is likely to cause a flaring up of the arc and consequent broadening of the lines, even if the arc does not go out, which it often does under such circumstances.

It has been suggested by Schuster[1] that this shift of spectral lines is possibly due to the "proximity of molecules vibrating in equal periods". If this supposition is correct then of course the shifts of the lines should be greater at any given pressure, as Schuster says the greater the amount of material used that produces them. However, many experiments both before and since the

1 Astrophysical Journal, April '96.

appearance of Jewell's paper show that this is not the case. Among the substances that have been most fully tested in this respect are iron, titanium, copper and zinc. The carbons used, though reasonably pure contained a considerable number of impurities in sufficient amounts to give some of their strongest lines and among these substances were iron, titanium and copper, each of which gave some very fine but quite measurable lines. The amounts of these substances were then gradually increased until they were as great as possible. In the case of iron, copper and zinc, solid rods of the metals were finally used but in every instance the shift of a given line of any substance remained constant for any definite pressure, showing that it depends upon the ab-

solute pressure and not upon the partial pressure of the gas or vapor forming the line in question.

More recently it has been suggested by Fitzgerald,[1] that a "vera causa for some shift towards the red in molecules emitting light" is the increase of the specific inductive capacity, due to increase of pressure, of the gas surrounding the arc. This is based of course upon the assumption, perhaps a correct one, that "electric forces are at least a part of the forces affecting the periods of vibration". The correctness of this suggestion has not been submitted to accurate experimental tests, nor does it seem very easy to do so, at least not

1 Astrophysical Journal, March '97.

directly, since the differences in the specific inductive capacities of gases are not sufficient to produce changes in the shifts greater than the errors of observation, even if the shifts are due entirely to the cause suggested. No matter what theory or suggestion is advanced it must be remembered that it is imperfect if it does not account in some way for the important fact that many elements produce two or more groups of lines differing greatly from each other in the magnitude of their shifts.

If, as many believe, the temperature of the electric arc is that of boiling carbon, it would seem natural to suppose that it would rise with increase of pressure. Very little seems to have been done to test this point, but a number of

experiments as conducted by Wilson[1] and later by Wilson and Fitzgerald[2] have given conflicting results. However, whether pressure causes an increase or a decrease of temperature, in either case the shifts of the spectral lines may conceivably be due to a change in temperature rather than pressure, and experiments were undertaken to clear up this point. In accordance with Wilson and Gray's[3] work, which indicates that the temperature of the negative pole is much less than that of the positive, a long arc, due to a fairly heavy current, was formed at right angles to the slit of the spectroscope, and one part of a photographic plate exposed

1. Proc. R. Soc. May 30, '95.
2. Astro. J. Feb. '97.
3. Proc. R. Soc. Nov. 24, '94.

to the spectrum due to the arc close to the positive and the other part to the spectrum as formed by the arc near the negative pole. No change however was detected in the position of the lines. Another method of testing the same point was to vary between wide limits the strength of the current used, since the temperature, according to Moissan[1], probably rises with increase of current. The extreme currents used were two amperes and ~~one~~ one hundred and eighty amperes respectively, but the positions of the lines appeared to remain absolutely unchanged. These experiments of course are only negative and do not settle the question, since the temperature of the electric arc, how it varies from point to point

1 Annales de Chemie et de Physique Oct. 1890. p. 231

and to what extent it is dependent upon the strength of the current and other conditions are not accurately known.

From the experiments described only this may be stated positively; that an increasing increase of pressure leads to an increase in the wave-lengths of many, probably of all, lines in the arc spectra of the elements.

The numerous negatives obtained, as well as the eye observations made, showed that the general effect of pressure was to broaden the lines and to bring out their reversals. However this was not always the case, since lines often appeared quite as fine and sharp at one pressure as at another, and in all probability this broadening of the lines was due chiefly at least to an increased density of the gas producing them, since it was always greater the greater the

amount of substance used. This idea is also in accord with Schuster's[1] observation that when gases are mixed in different proportions the lines of any one become sharper when it is present in smaller quantity, though the total pressure may remain the same.

The lines of the cyanogen bands came out more strongly under pressure, but never showed much if any shift, which fact furnishes conclusive evidence that the shifts of the other lines were real and not due to some disturbance of the apparatus, since they were all photographed simultaneously on the same plate, the cyanogen bands never being appreciably displaced while other lines were.

The shift or displacement of any line is

1. Ency. Brit. "Spectroscopy".

directly proportional to the excess of pressure above one atmosphere and is always towards the less refrangible or red end of the spectrum. (The same law has been shown by Mohler[1] to hold for pressures below one atmosphere.) This shift is very different for the lines of different elements, and also in many cases at least for different groups of lines of the same element. In particular the shifts of the lines of the several series (as given by the alkalies) principal, and subordinate are by no means equal even when the lines are of approximately the same wave-length, as shown by the tabulated results in Table I. Lines of the second subordinate series seem to be shifted about twice as much as those of the first, which in turn are displaced to an extent approximately twice that of the lines of the principal

1 Astrophysical Journal. Oct. '96.

series. A few iron lines, each of which is more hazy or softer, under pressure than the average line of this element, though in appearance indistinguishable from them at atmospheric pressure, are shifted about three times as much as other lines of the same substance. For the exact values observed see Table I. Another interesting case is furnished by the calcium line g, which is shifted about twice as much as the corresponding calcium lines H and K. The same thing is true also of the three corresponding lines of barium and of strontium.

Similar Lines of any given element, that is lines belonging to the same series, or to similar series, shift by amounts proportional to their wave-lengths. The most conclusive evidence of this proportionality was furnished by lines of different orders of spectra and

appeared on the same plate. Thus ultra violet lines of the third order were often found on the same plate with similar lines of the second of longer wave-length, but their measured shifts were approximately the same, and since the wave-length of a line of the third order is to that of one of the second that occurs at the same place as two to three, while the dispersion in the third order is to that in the second as three to two, it follows that constancy of measured shift means that it is proportional to wave-length. For the sake [illegible] of comparison it seemed advisable to reduce the shifts of all lines to what they would be at some definite wave-length, the one chosen being 4000 Ångström units, since most of the work was done in that neighborhood.

It should be stated that in some cases the values obtained for the shifts of the lines may have been due in a measure to unsymmetrical broadening; but this has certainly not led to much error, since, as already stated, only those lines were used which could be accurately measured, that is, those which were either comparatively narrow or else reversed.

Description of Table I.

The results of the measurements are given in Table I., in which the upper numbers in the line of each wave-length are the observed shifts in thousandths of an Ångström unit, and the lower their values

reduced to wave-length 4000. The different pressures used are given in atmospheres at the head of each column. As far as possible the wave-lengths are taken from Professor Rowland's table of solar wave-lengths, in process of publication in the Astrophysical Journal, and from a former table of his published in Astronomy and Astrophysics[1]. A few are taken from other sources, but it was necessary, for want of tables, to determine a number of them by comparison with known lines in their neighborhood, and since exact wave-lengths are not essential to this work, only such approximations of them are given as will serve to surely identify the lines in question.

1 A. and A., 12, 1893.

Table I.

Showing the pressures in atmospheres and the shifts of the given lines in thousandths of an Ångström unit, and the same reduced to wave-length 4000.

Aluminium

Wave-length	Pressure in Atmospheres										
λ	4	$4\frac{3}{4}$	6	7	$7\frac{1}{2}$	9	$10\frac{1}{2}$	$10\frac{3}{4}$	$11\frac{3}{4}$	$12\frac{3}{4}$	14
				38		38					
3082.27				50		50					
				40		38					
3092.84				52		50					
		17	29					44	49	48	68
3944.114		17	29					45	50	49	69
	17	25	26	37	36		44	40	57	52	76
3961.674	17	25	26	37	36		45	41	58	53	77
	17	21	28	38	36	38	44	42	53	50	72
Average	17	21	28	46	36	50	45	43	54	51	73

Several lines of the aluminium oxide band 4842–5041 were measured on two plates which were taken at different pressures. The lines were not particularly good, but the shift, if anything, was certainly slight.

Table I. – Continued

Antimony

Wave-length	Pressure in Atmospheres														
λ			$6\frac{3}{4}$												
			21												
3267.0			26												

Table I.— Continued

Arsenic

Wave-lengths λ	Pressure in Atmospheres														
					$8\frac{1}{2}$	9		10							
2898.83					20 28	18 25									
2860.54								20 28							
2780.30								22 32							
2745.09								20 29							
Average					20 28	18 25		21 30							

Table I.– Continued.

Barium

Wave-length	Pressure in Atmospheres						
λ	7	8	8½	10	10½	11	12
	45						78
4432.13	41						71
	36					56	69
4506.11	32					50	61
	32	52		56	68		80
5535.69 Group A.	23	38		40	50		58
Average	38	52		56	68	56	76
for group A	37	38		40	50	50	63
	23		24	32	34	40	
4554.271.	20		21	28	30	35	
			23	34			
4934.237 Group B.			19	28			
Average	23		24	33	34	40	
for group B.	20		20	28	30	35	
							117
3910.04							120
							119
3935.87							121
							126
3993.60							126
							135
4726.63 Group C							115
							124
Average							120

Table I. – Continued

Beryllium

Wave-length	Pressure in Atmospheres														
λ					$7\frac{1}{2}$										
3130.6					11 14										
3321.3					19 24										
3321.5					19 24										
Average					16 21										

Table I. Continued

Bismuth

Wave length	Pressure in Atmospheres														
λ						10				13½					
						26									
2898.18						35									
						34									
2989.15						45									
										48					
3397.31										57					
						30				48					
Average						40				57					

Table I. - Continued

Boron

Wave-length	Pressure in Atmospheres			
λ	8	$8\frac{1}{2}$	9	$9\frac{1}{4}$
	19	23	23	20
2496.867	30	37	37	40
	15	18	22	
2497.821	30	30	35	
	19	21	23	25
Average	30	34	36	40

Table I. Continued

Cadmium

Wave-length	Pressure in Atmospheres						
λ	7	7½	8	9	9½	10	10½
					18		
3261.17					22		
					20		25
3466.33					23		28
						20	
36[illegible]						22.	
[illegible]							
					19	20	25
Average					23	22	28

64[illegible] . For λ 4000 and 12 atmospheres Δλ = *80

* Mean of several concordant sets of observations by different [illegible] and at different pressures.

Table I. Continued.

Cadmium — Continued

Wave length	Pressure in Atmospheres.						
λ	7	7½	8	9	9½	10	10½
					29		25
3403.74					34		30
					27	18	20
3467.76					31	21	23
					16	19	
3613.04 1st Subordinate Series					18	21	
					24	19	23
Average					28	21	27
	40			60			
3081.0[illegible]	53			80			
	45			51			
3133.2[illegible]	60			65			
		31			47	56	
3252.63		38			57	69	
				54	79		
46[illegible].347				47	68		
			40	48	70		
4800.080			36	[illegible]	58		
	53	59	63	[illegible]	70		8[illegible]
5086.0[illegible] 2nd Subordinate Series	42	47	50	5[illegible]	56		66
	47	45	5[illegible]	50	67	56	82
Average	52	43	4[illegible]	5[illegible]	60	69	66

Only a few of the cadmium lines are particularly good.

Table I. Continued.

Caesium

Wave-length	Pressure in Atmospheres														
λ					6			7							
					138			123							
4555.44					121			108							
					95			78							
4593.34					82			68							
					117			101							
Average					102			88							

Table I. – Continued.

Calcium

Wave length		Pressure in Atmospheres.													
λ		3	4½	5	6	7	8	9	10	10½	11	12½	14½		
										25	24	28			
K 3933.825										25	24	28			
										22	26	33			
H 3968.625										22	26	33			
				13	18		29				31	30			
4283.169				12	17		27				29	28			
				16	17		20				35	40			
4289.525				15	16		19				33	38			
			8	17	13		22				35	34			
4299.[illegible]			8	16	12		20				33	32			
					12		27		24		31	30			
4302.[illegible]92					11		25		22		28	27			
					27						30				
430[illegible].11					25						27				
							27				30				
4318.80							25				27				
Lines of															
Small shift															
			8	15	17		25		24	24	30	33			
Average			8	14	16		23		22	24	28	31			
							42	47							
3158.[illegible]8							53	60							
							57								
3179.45							47								
							42		48		51	56	87		
g 4226.404							40		45		43	53	82		
						66		68			70				
5588.[illegible]35						47		49			50				
						66		80			72				
5594.691						47		57			52				
						68		74			63				
5598.[illegible]1						49		55			47				

Table I. — Continued.

Calcium — continued

Wave length λ	Pressure in Atmospheres: 3	4½	5	6	7	8	9	10	10½	11	12½	14½
5603.083						56 40						
4435.13										81 74		
4454.97 Lines of large shift.										80 73		
Average					67 48	~~44~~ ~~45~~	67 55	48 45		69 57	56 53	87 82
4425.61										84 76		
4435.86										88 80		
4456.08 1st Subordinate Series.										79 71		
Average										84 76		
6102.99	*67 44		*117 77			*166 109	*203 133					
6122.46	*53 35		*82 53			*140 91			*215 141			
6162.46 2nd Subordinate series.		*84 55					*148 96		*214 139			
Average	60 40	84 55	100 65			153 100	176 115		215 140			

* Eye observation.

Occur with lines of 1st subordinate series & shift to the same

Table I. — Continued

Carbon

Wave-length	Pressure in Atmospheres														
λ			8		8½		9		9¼		10				
			24		20		24		23		26				
2478.661			38		32		38		38		42				

A number of cyanogen lines were measured at various pressures, but did not seem to give any shift.

Table I. – Continued.

Cerium

Wave-length	Pressure in Atmospheres														
λ				6½			8								
				20											
3895.224				21											
				14											
3896.917				14											
				22											
3898.4				23											
				17											
3912.5				17											
				13											
3917.7				13											
				8											
3918.4				8											
				20											
3919.9				20											
				22											
3921.6				22											
				17											
3929.3				17											
				17											
3931.2				17											
				19											
3940.4				19											
				8											
3941.1				8											
							8								
3949.2							8								
				8											
3953.7				8											
				10											
3955.4				10											

Table I. - Continued.

Cerium - Continued

Wave length	Pressure in Atmospheres														
λ				6½			8								
							15								
3957.4							15								
				7											
3961.0				7											
				6											
3964.6				6											
				12											
3971.8				12											
				17											
3972.2				17											
				19											
3975.1				19											
				7			9								
3978.7				7			9								
				12											
3984.7				12											
				11											
3989.5				11											
				15			21								
3992.5				15			21								
				17											
3993.0				17											
				14			13								
Average				14			13								

Table I. Continued.

Chromium

Wave-length λ	Pressure in Atmospheres														
λ		4¾		6	7	9¾	10	10½	11	11½	12¼	12½	14	14½	
		4							26				36		
3886.942		4							27				37		
				16					20			12	29		
3919.309				16					20			12	30		
		7							33				32		
3941.637		7							34				33		
		7		12	16			23	27			36	47		
3963.831		7		12	16			23	27			36	47		
		14		12	12	25			28				38		
3976.839		14		12	12	[illegible]			28				38		
		12							34				41		
3984.059		12							34				49		
					19										
4026.318					19										
		3		9	19				26				26	30	
4254.505		3		9	18				24				24	28	
							17								
4266.894							16								
		14		11					31		24		40	31	
4274.958		13		10					29		22		38	29	
									30	23					
4280.556									28	22					
									34				41		
4289.885									32				44		
		9		14	16	25	17	23	29	23	24	24	38	31	
Average		9		13	13	25	16	23	28	22	22	24	37	29	

Table I. Continued

Cobalt

Wave length	Pressure in Atmospheres														
λ			9¾			11¼			12½			14½			
									19			33			
3354.510									23			39			
									18						
3361.413									22						
									20			22			
3395.016									24			26			
			17												
3405.255			20												
			14									23			
3409.336			16									27			
									23			29			
3417.384									27			34			
			18												
3461.326			21												
						20									
4121.476						19									
			16			20			26			27			
Average			19			19			24			32			

Table I.- Continued.

Columbium (Niobium)

Wave-length	Pressure in Atmospheres.														
λ					8½			9½							
								27							
3914.8								28							
								13							
3937.7								13							
					22			24							
4059.0					22			24							
					30			32							
4079.9					29			31							
					26			24							
Average					26			24							

Table I. Continued.

Copper

Wave length	Pressure in Atmospheres.														
λ			7			8			12¼		12½		13		13½
			8			7									
2883.03			11			10									
			11												
3010.92			15												
			9												
3036.17			12												
			7												
3073.89			10												
			13												
3094.07			17												
									25		28				28
3247.680									30		33				33
									20		32		30		36
3274.092									25		38		36		41
						13									
3317.28						16									
			11			11									
3337.95			13			13									
			8			14									
3476.07			10			16									
			12			17									
3483.82			14			19									
			16												
3520.07			18												
			12			19									
3524.31			14			21									
			15												
3533.8[illegible]			15												
			17												
3543.05			19												

Table I. Continued.

Copper continued.

Wave length λ	Pressure in Atmospheres.													
			7			8			12¼		12½		13		13½
			15			17									
3594.20			17			19									
			10												
3621.33			11												
			16												
3636.01			18												
			13												
3684.75			15												
						20									
5105.75						16									
Lines of small shift. Several others of this set were also measured.			12			15			23		30		30		32
Average			14			16			28		36		36		37
			27			28									
3365.46			32			33									
			24												
3371.52			28												
			36												
3620.47			40												
			35												
3741.32			38												
			35												
3860.54			37												
						43									
5218.45						33									
Lines of medium shift			31			36									
Average			35			33									

Table I. – Continued

Copper – continued

Wave Length λ	Pressure in Atmospheres		7			8
			87			
4177.87			83			
			57			
4249.21			54			
			64			
4275.32			60			
			81			
4378.40			74			
			80			
441[illegible]			73			
			74			
4[illegible]7.19			64			
						68
52[illegible].75						52
Lines of large shift. Several others belong to this set. most of these lines are "soft" & broad			74			68
Average			68			52
			50			
4480.58			44			
			53			
4531.04			46			
2nd subordinate series.			52			
Average			45			
						27
5[illegible]						21
						30
522[illegible].25						23
1st subordinate series						29
Average						22

Table I. Continued.

Erbium

Wave length	Pressure in Atmospheres														
λ							8								
							*30								
3988							30								

* The line measured was not very good.

Table I. — Continued.

Germanium

Wave-length	Pressure in Atmospheres														
λ				7			$8\frac{1}{2}$			9					
3039.198							22 29			24 31					
3269.628							24 29			22 27					
4226.724				30 28											
Average				30 28			23 29			23 29					

Table I. - Continued

Gold

Wave-length	Pressure in Atmospheres														
λ					7			10			10½				
					20			25			21				
4041.07					20			25			21				
					34			34							
4065.22					33			33							
											20				
3122.88											26				
											40				
3898.04											41				
											25				
3909.54											26				
					27			30			26				
Average					27			29			29				

Table I. - Continued.

Indium

Wave length λ			Pressure in Atmospheres. 7		9½		10		10½		11½		12½		14½
3256.17 No Series					19 23		23 28								
3258.66 1st Subordinate Series					36 44		37 45								
2932.71			43 60												
4102.000											69 68				
4511.345 2nd Subordinate Series					73 65		83 74		81 72				102 90		125 111
Average			43 60		73 65		83 74		81 72		69 68		102 90		125 111

Table I. — Continued.

Iridium

Wave-length	Pressure in Atmospheres.														
λ															

Table I.—Continued.

Iron

Wave-length	Pressure in Atmospheres														
λ	4¾	6	7	9	9¾	10	11	11¼	11½	12¼	12½	12¾	13	14	14½
								29							
3997.547								29							
			15			23	32								
4005.408			15			23	32								
						18									
4009.864						18									
	8	9						20							
4045.975	8	9						20							
								23							
4063.759								23							
						26									
4181.919						25									
						25									
4199.267						24									
						18									
4207.291						17									
						18									
4219.516						17									
	8		17				26								
4236.112	8		16				25								
			11			26	31				33	35		34	
4250.945			11			25	29				33	24		32	
	8	13	14				25	28	20	28	23	26		30	30
4271.934	8	12	13				23	26	19	26	22	24		28	28
						25									
4294.301						23									
						26									
4298.195						24									
								26				32	35	34	
4325.939								24				30	32	31	

Table I. Continued.

Iron – continued

Wave-length λ	Pressure in Atmospheres 4½	6	7	9	9½	10	11	11¼	11½	12¼	12½	12¾	13	14	14½
4377.948									21 19						
4382.928					17 16	24 22				26 24		27 25	35 32		31 28
4383.720					17 16				[illegible] [illegible]						
4404.127									23 21						
Group A.	8	11	14		17	23	29	25	23	27	29	28	35	32	31
Average	8	11	14		16	22	27	24	21	25	28	26	32	30	28
4222.382										70 66					
4227.606										77 73					
4233.772										79 75					
4236.112			26 25	59 56		60 57				79 75					
4250.287			57 54	95 90		84 80	81 77			78 74			86 81		
4260.647			47 45	72 68		66 63	69 65			74 70			86 81		
4271.934			59 56	98 92		74 70	82 77			84 79					
Group B			47	81		71	77			77			86		
Average			45	76		68	73			73			81		

Table I. – Continued

Lanthanum

Wave-length	Pressure in Atmospheres														
λ			8			9									
3921.695						21									
3929.363			13			33									
3949.199			26			24									
3995.877			21			35									
4[illegible].865			7			14									
4043.034			[illegible]												
4077.498			17												
40[illegible].[illegible]1			21												
Average			19			25									

Table I. Continued.

Lead

Wave-length λ	Pressure in Atmospheres 9	11	11¼	13½
				63
3639.728				70
				70
3683.622				76
	49	55	49	
4058.041	48	54	48	
	49	55	49	67
Average	48	54	48	73

Table I.– Continued

Lithium

Wave-length λ	Pressure in Atmospheres 2½	3	4	4½	5	5½	6	6½	7	8	9	9½	10	10½
Eye observations	*18	*24	*30				*66		*52					*130
6708.2	11	14	18				40		31	53	59			78
3232.77 Principal Series										66	7[illegible]			
Eye observations	*38	*37		*56		*[illegible]		*116				*177		
6103.77 1st Subsidiary Series	25	24		3[illegible]		50		7[illegible]				116		
										222				
4972.11 2nd Subsidiary Series										181				

* Eye observations

Table I. Continued.

Magnesium.

Wave-length λ	7½	8	8½	9	10	11	13
			Pressure in Atmospheres.				
			8	19			
2795.632			12	27			
			18	16			
2802.805			26	23			
No Series							
			13	18			
Average			19	25			
	12	6	29	27	23	21	29
*2852.239	17	9	40	39	32	30	37
				33	28		
3827.501				34	29		
				30	31		
3832.450				31	32		
				40	30		
3838.435				41	31		
1st subordinate series							
	12	6	29	32	28	21	29
Average	17	9	40	36	31	30	37
				66			
5167.497				51			
				62			
5172.856				48			
				47			
5183.791				56			
2nd subsidiary Series.							
				58			
Average				45			

* This line does not belong to 1st subordinate, but is near one that does.

Table I. – Continued.

Manganese

Wave-length	Pressure in Atmospheres.														
λ		4¾	6	7			10½	11	11¼	11½	12½	12¾	14		
			13	12							32	27	37		
4018.269			13	12							32	27	37		
		8						17							
4026.583		8						17							
									19			33	34		
4030.947									19			33	34		
		8	18	13								26	32		
4035.883		8	18	13								26	32		
									20						
4061.881									20						
		10		22											
4235.298		10		21											
		8		18			27	37				32	36		
4235.450		8		17			25	34				29	33		
		13	21							31	48		47		
4239.890		12	20							29	45		44		
		14	21	22			25	39				47	47		
4257.815		13	20	21			23	36				43	43		
		14	20	22			38			40	41	40	46		
4266.081		13	19	21			35			37	38	37	43		
		10		21			37	43		39	41	38	44		
4281.257		7		20			34	40		36	38	35	41		
		12													
4284.223		11													
		11	19	19			32	34	20	37	40	35	40		
Average		10	18	18			30	32	20	34	38	33	38		

Table I. — Continued

Mercury

Wave length λ	Pressure in atmospheres 10	11
	63	63
3650.3	70	70
	?r	
2nd Sub. 5461.0	66	
	77	63
Average	68	70

Table I. — Continued

Molybdenum

Wave length	Pressure in Atmospheres														
λ					9			11½							
3132.749								31 40							
3158.3								27 34							
3170.5					28 33			32 40							
3194.2					18 22			33 41							
Average					23 28			31 39							

Table I. - Continued.

Neodymium

Wave-length	Pressure in Atmospheres														
λ							9								
							18								
4279.874							17								
							7								
4281.0							7								
							6								
4284.8							6								
							7								
4302.7							7								
							12								
4319.1							11								
							5								
4334.5							5								
							11								
4348.0							10								
							5								
4362.2							5								
							15								
[illegible].8							14								
							14								
[illegible]1.0							13								
							6								
4420.7							5								
							14								
4421.3							13								
							8								
442[illegible].5							7								
							10								
443[illegible].0							9								
							10								
Average							9								

Table I.– Continued

Nickel

Wave-length	Pressure in Atmospheres														
λ					9¾			12½			14½				
3391.180								14 17							
3413.637								19 23							
3414.092								19 23							
3437.447					20 23						34 39				
3458.606								27 31			29 33				
3461.322					16 18			23 25							
3500.993								24 27			35 40				
3515.207								34 38			41 45				
3524.677								30 35							
5155.937					24 18										
Average					20 20			24 26			35 39				

Table I.— Continued.

Osmium

Wave-length	Pressure in Atmospheres.														
λ					$12\frac{3}{4}$		13								
							17								
4260.993							16								
					20		18								
4420.633					18		16								
					20		18								
Average					18		16								

Table I. - Continued.

Palladium

Wave length	Pressure in Atmospheres														
λ			12			13½									
						33									
3373.139						39									
						46									
3404.725						47									
			17			38									
3421.367			20			44									
						31									
3433.578						36									
						31									
3441.539						36									
			18			27									
3460.884			21			31									
			21			25									
3481.300			24			29									
			19			30									
3489.915			22			34									
			22			44									
3609.696			24			48									
						41									
3634.841						45									
			17			28									
3690.483			19			31									
			19			33									
Average			22			38									

Table I. – Continued

Platinum

Wave-length λ	Pressure in Atmospheres 12¼	12¾	13	14½
			16	
2830.41			22	
			14	
2893.98			20	
			12	
2897.99			17	
		12	17	
2929.91		16	24	
	15	17	18	13
2998.079	20	23	25	18
			18	23
3042.745			25	32
				16
3064.82				21
	25		31	
4442.723	23		28	
	20	15	18	18
Average	21	20	23	24

Table I.—Continued.

Potassium.

Wave-length	Pressure in Atmospheres													
λ					8			9						
					76			93						
4044.294					75			92						
					88			106						
4047.338 Principal Series					87			105						
					82			99						
Average					81			98						

Table I. - Continued.

Praseodymium

Wave-length λ	Pressure in Atmospheres														

Table I. — Continued.

Rhodium

Wave-length	Pressure in Atmospheres.								
λ		12	$12\frac{1}{4}$	$12\frac{3}{4}$	13	$14\frac{1}{2}$			
4211.304			31	38	45 43 45	37			
4374.981		17	28	34	41	34			
3399.839		20 23							
3412.417		27 16							
3435.039		19 19							
3462.184		21 20							
3474.920		23 22							
3479.053		25 21							
3502.674		24 26							
3507.466		29 16							
3626.744		18 15							
3658.135		17 [illegible]							
3666.366		25 27							
3690.853		29							
Average		20 23	31 28	38 34	45 42	37 34			

Table I.— Continued.

Rubidium

Wave-length.	Pressure in Atmospheres.														
λ					8			8½							
4201.98					73 70			123 117							
4215.72					75 71			88 84							
Average					74 71			106 101							

Table I. — Continued.

Ruthenium

Wave-length	Pressure in Atmospheres.														
λ							12.								
3429.689							24 34								
3499.095							26 30								
3593.178							21 23								
3599.914							27 30								
3625.339							32 36								
3635.084							20 22								
3637.612							25 28								
3661.525							33 36								
3663.520							17 19								
3669.688							23 25								
3678.456							20 22								
3727.073							25 27								
3728.173							21 23								
3730.577							33 36								
Average							25 28								

Table I. -- Continued

Scandium

Wave-length	Pressure in Atmospheres														
λ								12							
								22							
4247.0								21							
								30							
4314. 3								28							
								26							
4320.9								24							
								26							
Average								24							

Table I. — Continued

Silicon

Wave-length λ	Pressure in Atmospheres 8½	9	9½	10	11	11½	12
2506.994	13 21						
2516.210	12 19						
2519.297	18 28						
2524.206	13 21						
2528.599	22 34						
2881.695	20 28	21 29		25 35	31 40		
3905.660	-		31 32		44 45	40 41	39 40
Average	16 25	21 29	31 32	25 35	38 43	40 41	39 40

Table I.— Continued.

Silver

Wave-length λ	Pressure in Atmospheres.													
			8		$9\frac{3}{4}$		$12\frac{1}{2}$		13					
3280.80			29 34		28 33		32 39							
3383.00					34 40		27 32		32 38					
Average			29 34		31 37		30 36		32 38					

Table I. — Continued.

Sodium

Wave-length. λ	Pressure in Atmospheres.													
			3	3½	6½	7	7½	8	8½	9	10½			
								47	67					
3302.504								57	81					
								61	57					
3303.119								74	70					
			*30		*69	62				94	*121			
D_2 5890.182			20		47	42				62	82			
				*25	*63	78				122	*116			
D_1 5896.154				17	43	53				83	79			
Principal Series														
			30	25	66	70		54	62	108	119			
Average			20	17	45	48		66	76	73	81			
							314	*400		426				
5682.861							221	280		300				
			*100	*130			368	*345		460				
5688.434			70	91			259	242		323				
2nd Subordinate Series														
			100	130			341	373		443				
Average			70	91			240	261		312				

* Eye observations.

Table I.—Continued.

Strontium

Wave-length λ	Pressure in Atmospheres.													
			8½		10		10½		11		11½		12	
									26		[illegible]			
4077.885			28				34		26 / 34		[illegible] / [illegible]			
4215.703			27				[illegible]		[illegible] / 42		43 / 37			
4742.07									36 / 42		31 / 35			
4784.43									35 / 23		29		29	
4812.01									19 / 50		48		24	
4832.23									4[illegible] / 40		40 / 40			
4876.35							46		33		33			
5222.43							35 / 60							
5225.35							46 / 44							
5229.52							34 / 45							
5238.76							34 / 60							
5257.12							46							
Group A.			28				48		[illegible]		41		29	
Average			27				38		32		36		24	

Table I. — Continued

Strontium — Continued

Wave length	Pressure in Atmospheres.														
λ			8½		10		10½		11		11½		12		
							53								
3351.35							63								
							57						71		
3380.89							67						83		
													78		
3404.58													89		
			46		57				53				93		
4607.510			40		50				46				81		
									40				83		
4962.45									72				66		
Group B.															
			46		57		55		72				81		
[illegible]			40		50		65		59				80		

Table I. – Continued.

Tantalum

Wave-length	Pressure in Atmospheres														
λ							12								
3918.6							13								
3922.9							19								
3931.1							11								
3970.3							16								
3982.1							18								
3988.9							23								
4003.9							14								
4007.0							14								
4022.1							18								
4030.1							21								
4061.6							15								
4064.8							20								
4105.2							18								
Average							17								

Table I.– Continued.

Thallium

Wave-length	Pressure in Atmospheres.														
λ				9½				11							
1st Subordinate 3519.342				49 56				*87 99							
1st Subordinate 3529.58								*75 86							
Average				49 56				81 93							

* Measurements of good lines.

Table I. – Continued.

Thorium

Wave length λ	Pressure in Atmospheres 8	9
	12	15
4248.1	11	14
	14	
4283.7	13	
	7	
4381.6	7	
	9	8
4391.3	8	7
	14	11
4433.2	13	10
	15	
4439.3	14	
	15	20
4441.1	14	18
	21	12
4465.5	19	11
	4	
4487.7	4	
	21	
4510.7	19	
	13	13
Average	12	12

Table I. – Continued

Tin

Wave length	Pressure in Atmospheres.														
λ				$9\frac{3}{4}$	10	$12\frac{1}{2}$		13		$14\frac{1}{2}$					
						43				54					
3175.12						39				63					
				37		47		44		51					
3262.44				46		[illegible]		55		63					
						44				64					
3330.71						53				[illegible]					
					20										
2706.61					30										
					40										
2812.70					57										
					24										
2840.06					34										
					24										
2850.72					34										
					25										
2863.41					35										
					31										
3009.24					41										
					22										
3032.88					30										
					36										
3034.21					48										
				37	28	48		44		58					
Average				46	39	58		55		69					

Table I.— Continued.

Titanium

Wave-length λ	Pressure in Atmospheres. 8	8½	9	10	10½	11	11½
	20						
3186.564	25						
	22	21					
3192.120	27	26					
	18	25					
3200.034	22	31					
	15						
3222.970	19						
	12						21
3234.635	15						26
	13						18
3236.703	16						22
	13						22
3239.170	16						27
	12						15
3242.125	15						18
		17					
3254.314		21					
		14					
3326.907		17					
	15	15					19
3341.967	18	18					23
					14		17
3349.043					17		20
		7			14		
3361.327		8			16		
		9			15		
3372.901		10			18		
		16					
3380.397		19					

Table I. – Continued

Titanium – Continued

Wave-length λ	Pressure in Atmospheres	8	8½		9		10		10½		11		11½		
3900.681			17 17												
3904.926			15 15												
3913.609			15 15												
3924.673			13 13												
3930.022			9 9												
3947.918			10 10												
3948.818			9 9		19 19										
3956.476			11 11		13 13								18 18		
3958.355					16 16										
3981.917					18 18										
3989.912					15 15								16 16		
3998.790											15 15		22 22		
4009.079			13 13												
4024.726			15 15												
Average		16 19	14 15		16 16				14 17		15 15		19 21		

Table I. Continued

Tungsten

Wave-length λ	Pressure in Atmospheres														
					$9\frac{1}{2}$			11							
					20			13							
4009.0					20			13							
								15							
4074.7								15							
					20			14							
Average					20			14							

Table I. Continued

Uranium

Wave-length λ	Pressure in Atmospheres 9½	11	12
			12
3886.4			12
	4	3	
3993.6	4	3	
		5	
3912.7		5	
		4	
3916.0		4	
	7	11	14
3932.2	7	11	14
		7	
3951.5		7	
		6	
3954.9		6	
		4	
3982.6		4	
		5	
3986.0		5	
		13	
3987.6		13	
		12	
3989.7		12	
		10	
4050.3		10	
		13	
4064.6		13	
	6	8	13
Average	6	8	13

Table I.—Continued

Vanadium

Wave-length	Pressure in Atmospheres														
λ					8				10						
					5										
3902.399					5										
					9				13						
3910.984					9				13						
					14				17						
3913.0					14				17						
									23						
3914.5									24						
					13										
3922.560					13										
					22										
3924.8					22										
					12				18						
3925.4					12				18						
					14										
3928.1					14										
					5										
3934.2					5										
					18				19						
3937.7					18				19						
									20						
3938.3									20						
					26				23						
3939.5					26				23						
									15						
3950.4									15						
					17				17						
3979.6					17				17						
					16				15						
3984.5					16				15						
					21				24						
3984.7					21				24						

Table I. – Continued

Vanadium – Continued

[illegible]	Pressure in Atmospheres														
λ					8				10						
					12				22						
3989.0					12				22						
					22										
3990.712					22										
					15										
3992.971					15										
					14										
3998.9					14										
					17										
4042.8					17										
					16										
4051.204					16										
					19										
4051.491					19										
					24										
4057.2					24										
					10										
4092.821					10										
					23										
4105.318					23										
					17										
4120.6					17										
					18										
4123.539					17										
					19										
4128.251					18										
					13										
4132.100					13										
					[illegible]										
4134.589					21										
					16				14						
Average					16				19						

Table I.— Continued

Yttrium

Wave-length λ	Pressures in Atmospheres: 4⅔		6		7		10		11		12½		13	
3950.497	5	5	7	7					15	15	17	17	14	4
3982.742	4	4			4	4					17	17	18	18
4309.780							10	11						
4358.892							16	17						
4375.110							19	21						
4398.185							21	23						
4422.760							18	20						
Average	5	5	7	7	4	4	17	18	15	15	17	17	16	16

Several other lines were measured, and found to agree quite well with the above.

Table I. — Continued

Zinc

Wave-length	Pressure in Atmospheres		
λ	7	8	11½
3075.99	12 16		
3302.67		30 36	31 37
~~3303.03~~			
3345.13		26 30	32 38
~~3345.62~~			
3346.04		30 36	
No Series			
Average	12 16	29 34	32 38

Table I. Continued

Zinc — Continued

Wave-length λ	8	$9\frac{3}{4}$	$11\frac{1}{2}$	$12\frac{1}{4}$	$13\frac{1}{2}$
Pressure in Atmospheres					
3282.42	27 / 33		32 / 39		
3303.03	22 / 27		37 / 44		
3345.62	25 / 30		33 / 31		
1st Subordinate Series Average	25 / 30		34 / 41		
3018.50	46 / 62				
3035.93	44 / 58				
3072.19	49 / 64				
4680.17	61 / 52	68 / 58	60 / 51		
4722.341	51 / 43	62 / 52	77 / 63	58 / 49	65 / 53
4810.724	56 / 47		68 / 57	67 / 56	74 / 62
2nd Subordinate Series Average	51 / 54	65 / 55	68 / 57	63 / 53	69 / 58

Table I.— Cont'd

Zirconium

Wave-length	Division in Al spectrum														
λ						9									
						13									
3958.355						13									
						24									
3999.117						24									
						23									
4029.796						23									
						20									
Average						20									

A. The Relations of the Shifts to each other and to Certain Properties of the Elements.

As already stated, at least many elements produce lines whose shifts for the same wave length are quite different, but this difference is by no means a hap hazard one. Thus any series (as described by Kayser and Runge) of lines produced by an element give shifts which, when reduced to the same wave-length, are approximately equal; while apparently, the shifts of the series, principal, first and second subordinate are to each other respectively as one to two to four. As is well known lines of any series of a given element are quite like unto each other in general appearance, but very different from those of other series, and the same

is true of the several pairs of lines of iron and copper, for instance, which have such different shifts. In general then it appears that lines of the same character of any element, when reduced to the same wave-length, give equal shifts, which nevertheless may differ widely from those of a different character though of the same element.

Lines of the same series, not only of a given element but also those of different elements, resemble one another closely, and consequently in comparing shifts of lines with other properties of substance it is necessary to confine ones attention as far as possible to lines of the same character; and in accordance with this notion the following relations may be derived as shifts of what ought to be found the most characteristic.

lines of the respective elements, that is those lines which are the easiest to obtain (at least in the arc spectra) and which produce the sharpest reversals, and consequently admit of the most accurate measurements.

On forming, for various elements, the product of the cube root of the atomic volume (i.e. quotient of atomic weight divided by density) and the coefficient of linear expansion of the substance in the solid form, certain numbers are obtained whose ratios are approximately those of the shifts of the lines of the respective elements. This is shown in table II. in which the atomic volume and coefficient of expansion both refer to 40°C. and the shift to a pressure of twelve atmospheres and wave-length 4000.

A similar expression is used by Raoul Pictet in his formula for deducing the melting points of the metals.

He finds that the continued product of the absolute temperature of the melting point, the coefficient of linear expansion of the substance in the solid state and the cube root of the atomic volume is nearly the same for all metallic elements except antimony and bismuth. Table II. also shows the relation between Pictet's results and the shifts of the lines, by giving the quotients obtained by dividing a constant, namely 1.5000, by the absolute melting points of the elements. The number 1.5000 was chosen to reduce his results to numbers comparable with the shifts at twelve atmospheres; that of iron being made to coincide with the value given by the product of its coefficient of linear expansion by the cube root of its atomic volume. It appears that the shifts

are about as near the absolute lengths as are the melting points, and consequently [illegible] since the product of the weight by the absolute melting point is nearly constant, or what amounts to the same thing the weight is inversely proportional to the absolute temperature of the melting point.

Description of Table II.

The first column gives the symbols of those elements some of whose lines have been examined. Under W are their atomic weights, and in the next column marked $\sqrt[3]{W}$ are the cube roots of these weights. Under V are the atomic volumes at 4°C and under α the coefficients of linear expansion

at the same temperature. The column marked 'T' gives the absolute temperatures of the melting points, and that marked $\frac{45000}{T}$ the quotients indicated. Under δ' are the shifts at twelve atmospheres and wave-length 4000, and the last column, marked $\alpha\bar{W}$, gives the product of the coefficient of linear expansion and cube root of atomic volume multiplied by 10^6. The values of the atomic weights, atomic volumes and melting points have been taken, as far as possible, from Nernst's Theoretical Chemistry, and the coefficients of expansion from the Physikalisch Chem. Tabellen von Landolt und Börnstein.

In a few cases more recent and possibly more accurate values of the above constants have been obtained, but the difference is not sufficient to alter my results.

Table II.

Element	Atomic weight W	$\sqrt[3]{W}$	Atomic volume V	Coefficient of linear expansion λ	Temperature of melting point T	$\frac{43600}{T}$	Shift S	$\lambda\sqrt[3]{V}$
				.0000				
Al	27.04	3.00	10.6	2313	1123	43.3	55	30.6
Sb	119.6	4.93	17.9	1692 } 0882	710	68	49	43 } 23
As	74.9	4.22	13.2	0559	>773	<63	39	13
Ba	136.9	5.15	36.5	?	748	65	58 } 34	?
Be	9.03	2.09	4.9	?	>1270	<34	36	?
Bi	207.5	5.92	21.1	1621	538	90.3	49	44.7
B	10.9	2.22	4	?	?	?	49	?
Cd	111.7	4.[illegible]	12.9	3069	593	[illegible]	76	75.6
Cs	132.7	5.10	[illegible]	?	?	?	161	?
Ca	39.91	3.42	25.[illegible]	?	>Sr	<Sr	27 } 54	?
C	11.97	2.29	3.6	0118 } 0540 } 07[illegible]	?	?	0 } 50	?
Ce	139.9	5.19	21	?	<1275	> [illegible]	27	?
Cr	[illegible]	3.74	7.7	?	?	?	[illegible]	?
Co	[illegible]	[illegible]	6.9	12[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cb	93.7	[illegible]	13.0	?	?	?	33	?
Cu	63.1[illegible]	[illegible]	7.1	1678	1330	[illegible]	[illegible]	[illegible]

Table II. — Continued

Element	Atomic weight A	$\sqrt[3]{A}$	Atomic volume V	Coefficient of linear expansion α	Temperature melting point T	$\frac{48600}{T}$	Shift S	×$\sqrt{V}$
				.0000				
Er	166	5.50	?	?	?	?	47	?
Ge	72.3	4.17	13.2	?	?	?	44	?
Au	196.7	5.82	10.1	1443	1310	37	40	67
In	113.6	4.84	15.3	4170	449	108.3	88	103.5
Ir	192.5	5.77	[illegible]	0700	2223	22		14
Fe	55.9	3.82	7.2	1210	2080	23.3	25	[illegible]
La	138	5.17	22.5	?	>710	<69	32	?
Pb	206.4	5.91	18.1	2924	605	80.3	60	76.9
Li	7.01	1.92	12.9	?	453	107	85	?
Mg	24.3	2.90	13.9	2694	1023	47	62) 44) 30	65
Mn	54.8	3.80	6.9	?	2170	22.9	33	?
Hg	199.8	5.85	14.1	6000	233	209	81	145
Mo	95.9	4.58	11.1	?	?	?	40	?
Nd	142.1(?)	5.22	?	?	?	?	11	?
Ni	58.6	3.88	6.7	1279	1870	26.5	28	34
Os	190.3	5.76	8.5	0657	2770	17.5	17	[illegible]
Pd	106.35	4.74	9.2	1176	1775	27.4	27	[illegible]

Table II. -- Continued

Element	Atomic weight W	$\sqrt[3]{W}$	Atomic volume V	Coefficient of linear expansion α	Temperature of melting point T	$\frac{48600}{T}$	Shift S	$\alpha\sqrt[3]{V}$
				.0000				
Pt	194.3	5.79	9.1	0899	2050	23.7	20	18.5
K	39.03	3.40	45.4	8415	335	145	132	300
Pd								
Rh	104.1	4.70	8.6	0850	2270	21.4	25	17.4
Rb	85.2	4.40	56.1	?	311	156	132	?
Ru	103.5	4.70	8.4	0963	2070	23.5	28	20
Sc	43.97	3.52	17(?)	?	?	?	24	?
Si	28.3	3.05	11.4	0763	?	?	43	17
Ag	107.7	4.76	10.2	1921	1230	39.5	39	42.2
Na	23.0	2.84	23.7	7105	369	132	108	204
Sr	87.3	4.44	34.9	?	> Ba	< Ba	35 } 70 }	?
Ta	182	5.67	16.9	?	?	?	17	?
Tl	203.7	5.89	17.2	3021	563	86.3	102	78
Th	232.	6.15	20.9	?	?	?	18	?
Sn	118.8	4.92	16.3	2234	503	96.6	55	50.6
Ti	48.0	3.63	13(?)	?	?	?	22	?

Table II. – Continued

Element	Atomic weight W	$\sqrt[3]{W}$	Atomic volume V	Coefficient of linear expansion α	Temperature of melting point T	$\frac{48600}{T}$	Shift S	$\alpha \sqrt[3]{V}$
				.0000				
W	183.6	5.68	9.6	?	?	?	19	?
U	239.0	6.20	12.6	?	?	?	11	?
V	51.1	3.71	9.3	?	?	?	25	?
Y	88.9	4 46	?	?	?	?	15	?
Zn	65.10	4.02	9.1	2918	676	71.9	57	61.2
Zr	90.4	4.49	21.7	?	?	?	28	?

Like many other properties of the elements the shifts of the lines is also a periodic function of the atomic weight, as is clearly seen in the line of shifts as plotted on Plate III. The abscissae are atomic weights and the ordinates the shifts corresponding to the respective elements. The maxima fall, as do those of the atomic volumes, on the alkali metals, lithium, sodium, potassium, rubidium and caesium.

As shown by the results tabulated in Table II. those elements like sodium, potassium, indium, thallium cadmium &c which have very large coefficients of linear expansion also have the largest shifts, and the converse is equally true. The one approach to regularity however in this respect is with elements of the same group. In several cases the shifts seem to be proportional roughly to their coefficients of linear expansion, as is the case with sodium and potassium; tin and lead; aluminium, indium and thallium &c.

Another and somewhat simple relation is this: The shifts of the spectral lines of similar elements, in the main those of the right or left half, as commonly tabulated, of a Mendeleeff group, are generally proportional to the cube roots of the atomic weights of the elements that produce them. This is shown in Table III. in which it will be seen that the observed and calculated values agree quite closely except in very few cases. The single carbon line shifts about twice the calculated amount, and the lines of a few other elements, platinum, osmium &c only about half as much as would be expected. It may be that in these cases lines comparable to those measured of the other elements have not been selected, however this is by no means certain. The lines measured of neodymium and uranium shift much less than the calculated amounts.

Whether this is true of all the numerous lines of these two elements I am unable to say.

Description of Table III.

Each horizontal row of Table III. contains first the symbol of a certain element, followed by the observed shift of its lines in thousandths of an Ångström unit for twelve atmospheres and wave-length 4000: then the symbol of an element of the same group followed by the calculated shift of its lines, and finally the observed shifts of the same lines. The shifts marked standard are assumed to be correct, and each marked calculated deduced from the standard of the same horizontal row on the assumption that they are to each other as the cube roots of their respective atomic weights.

Table III.

Showing shifts in thousandths of an Ångström unit for twelve atmospheres and wave-length 4000.

Standard		Calculated		Observed
Cs	161	Li	60	85
Cs	161	Na	90	108
Cs	161	K	109	132
Cs	161	Rb	139	132
Cu	33	Ag	39	39
Cu	33	Au	48	40
Ca	54, 27	Mg	46, 23	62, 44, 30
Ca	54, 27	Sr	70, 35	65, 37
Ca	54, 27	Ba	81, 40	58, 34
Zn	57	Be	30	36
Zn	57	Cd	68	76
Zn	57	Hg	53	51
La	32	Y	25	15
La	[illegible]	[illegible]	22	24
Al	55	[illegible]	40	49
Al	55	[illegible]	89	[illegible]

Table III. — Continued

Standard		Calculated		Observed
Ai	55	Tl	106	102
Ti	22	Zr	26	28
Ti	22	Ce	30	27
Ti	22	Th	35	18
Sn	55	C	26	50
Sn	55	Si	34	43
Sn	55	Ge	47	44
Sn	55	Pb	66	60
V	25	Cb (Nb)	28	34
V	25	NDi (?)	35	11
V	25	Ta	38	17
Bi	49	As	35	38
Bi	49	Sb	41	49
Cr	26	Mo	32	40
Cr	26	W	40	19
Cr	26	U	43	9
Bi	49	E	45	47

Table III. Continued

Standard		Calculated		Observed
Fe	25	Ru	36	28
Fe	25	Os	38	17
Ni	28	Pd	34	27
Ni	28	Pt	42	20
Co	24	Rh	29	25
Co	24	Ir	36	

In determining the groups of similar elements I have been guided in some measure by their spectra, and since the grouping adopted is not exactly, though very nearly, that which is commonly made I have thought it necessary to give it in Table IV. It will be seen that sodium, for instance is classed with lithium, potassium rubidium and caesium which it strongly resembles spectroscopically rather than, as is often done, with copper silver and gold which it does not resemble in this respect. Again and for similar reasons, magnesium is classed with calcium, strontium and barium, rather than with zinc cadmium and mercury. In one case however is there a change of an element

from one to another of the Mendeleeff groups, and besides the right and left halves as usually tabulated are in the main retained, the only changes being with elements of small atomic weights which have many properties in common with each half of their groups and which are often regarded as common to the two halves. Thus, as just stated, magnesium is placed with calcium strontium and barium because spectroscopically it resembles them rather than zinc cadmium and mercury, though it has so many properties in common on the one hand with those of calcium, strontium and barium, and on the other with those of zinc, cadmium and mercury that it might very well be classed with either.

Table IV.

Showing the groups adopted of similar elements.

Group I.		Group II.		Group III.		Group IV.		Group V.		Group VI.		Group VIII.		
Li	Cu	Mg	Be	Sc	B	Ti	C	V	As	Cr		Fe	Ni	Co
Na	Ag	Ca	Zn	Y	Al	Zr	Si	Cb	Sb	Mo		Ru	Pd	Rh
K	Au	Sr	Cd	La	Ga	Ce	Ge	Ndi?	Bi	W.		Os	Pt	Ir.
Rb		Ba	Hg		In	Th	Sn	Ta		U				
Cs					Tl		Pb							

Summary of results

The following list of relations between the shifts of spectral lines, the conditions under which they are produced and the properties of the elements producing them is probably far from perfect. Some of them may be more or less accidental, and in all probability others quite as important have been overlooked. However I have not searched at all carefully for such relations, but have noted those which have forced themselves upon me, hoping that by so doing I may be of service to any one who should attempt to explain the observed phenomena.

These relations are:

1. With increase of pressure all isolated lines are shifted towards the red end of the spectrum.

2. This shift of the lines is directly proportional to the increase of pressure.
3. The shift does not depend upon the partial pressure of the gas producing the lines but upon the total pressure.
4. It seems to be independent of temperature.
5. The lines of bands (at least of the cyanogen and aluminium oxide bands) are not appreciably shifted.
6. The different series of lines of a given element are shifted differently, seemingly, when reduced to the same wave-length, in the ratios of one to two to four respectively, for the principal, first and second subordinate series.
7. Similar lines of an element, though not belonging to a recognised series, are shifted equally (when reduced to the same wave-length), but to a different extent than are those unlike them.

8. The shifts of similar lines of a given element are to each other as their wave lengths. (This is but a restatement of the first part of 7. but its importance will, I trust, justify its repetition in the above form).

9. The shifts of similar lines of different elements are to each other (for the most part) inversely as the absolute temperatures of their melting points.

10 The shifts of analogous lines are to each other approximately as the products of the coefficients of linear expansion and cube roots of the atomic volumes of the respective elements to which they are due.

11 Analogous lines of similar elements shift proportionally to the cube roots of the respective atomic weights.

12. Substances which, in the solid form, have the greatest coefficients of linear expansion have also the greatest

shifts of their spectral lines, the converse statement is equally true.

13. The shifts of analogous lines are periodic functions of atomic weight and consequently may be compared with any other property of the elements which itself is a periodic function of their atomic weights.

The observations upon which the above conclusions are based, though very numerous, are by no means as complete as could be desired and I feel quite certain that a more searching examination of a larger number of lines, probably at considerably higher pressures (in which case a current of moderately high voltage will be required) will add materially to our knowledge of the interesting relations between the spectral lines and the conditions under which they are produced.

Discussion of Results.

How to interpret the shifts of the lines and their relations to each other and to other properties of the elements that produce them is not very evident. Presumably though the light waves are due either to elastic vibrations or else to electric oscillations of the particles generating them.

Consider then an isolated body, to be definite a rectangular bar of steel say, producing elastic vibrations. Waves of different lengths may be given off simultaneously but the length of each will be proportional to the length of the segment producing it. If the linear dimensions of the bar be increased, the other properties remaining unchanged, the wave-length of each set of vibrations will be correspondingly increased, the total increase in each case being directly proportional

to the wave-length itself. Now suppose the bar in the midst of a great number of others of either the same or of different material and all moving at random with a considerable velocity. Many collisions will take place; part of the energy of the system becoming internal energy of the bar in question and thereby increasing its linear dimensions, and consequently the wave-lengths of its vibrations. Further, the more numerous the bars in a given space, the more frequent in the same proportion will be the collisions and therefore the greater will become the internal energy of the bar, its linear dimensions and the wave-lengths of its vibrations. Again, of two bars under the supposed conditions, that one which has the greater coefficient of linear expansion will suffer the greater change in the lengths of

its wars.

Since the coefficient of expansion of a bar of metal remains constant, so far as we know, no matter how small it be made, and since also the coefficient of expansion of a porous bar, or one bored in any directions and to any extent is the same as that of a solid bar of the same substance, it would seem, on pushing these ideas to the limit, that the coefficient of expansion of a substance in the solid form is also more or less closely a measure of the expansion of its smallest parts or molecules. Nor does it seem unreasonable to suppose, when these molecules are moving more or less freely as they are when the substance is in the form of a gas, that their

collisions would lead to more or less internal energy of the molecules themselves and consequently to their expansion and to an increase in the wave-lengths of their vibrations. At any rate if the particles producing light vibrations have properties like those of appreciable masses of the same substance, then the above considerations in regard to the steel bar offer a possible explanation of many, and probably the most important, of the observed facts in regard to the shifts of spectral lines. In this way is explained why the wave-lengths should always increase with increase of pressure, why this increase of wave-length is proportional to the increase of pressure, and why it is independent of the partial pressure of the gas to which the lines are due. It is also evident that the

shifts of the lines should be proportional to their wave-lengths, and greatest for those substances which have the greatest coefficients of linear expansion. In accordance with this idea the shift of the lines should be, as experiment shows them, practically independent of temperature when the pressure is kept constant, since in this case the greater velocity of the particles due to increase of temperature is offset by the corresponding expansion, so that the increase of internal energy of the molecules due to collisions is not sensibly affected by change of temperature alone.

The different series of lines [illegible] equally displaced by [illegible], and it is with the greatest hesitation

that I venture to make the slightest suggestion. Conceivably the vibrating particles may expand differently in different directions, or possibly the different series of lines may be due to entirely different molecular complexes of very different coefficients of expansion. This latter idea seems in a measure supported by the following considerations: The melting point of a substance and its coefficient of expansion seem to be in some sense inversely proportional to the ability of its particles to resist external influences; and those molecular complexes least capable of resisting external influences may therefore, at the temperature of the electric arc, be subject to dissociation and possibly to other changes as well. Now it happens that those substances which furnish clearly marked series of lines,

as do sodium, potassium, cadmium, mercury and others are just those whose melting points are among the lowest and whose coefficients of expansion are the greatest. Should dissociation take place it is clear that the dissociated parts must be either less subject to external influences or else less powerfully acted upon than are the undissociated parts else they would still further dissociate, which process must surely stop somewhere. In either case a smaller coefficient of expansion of the parts is to be expected, than is that of the undissociated portions. Again it seems but natural to suppose the dissociation taking place along planes of symmetry should such planes exist or at least in a manner that would leave the parts with linear dimensions approximately [illegible]

the original [illegible]. Supposing then the coefficients of expansion, or better possibly, the amounts of energy used up in producing expansion of the parts to be such as to cause these coefficients to be to each other as the linear dimensions of the particles themselves, [illegible] to form relation of the shifts of the series.

This also suggests why elements analogous to each other, like rubidium and caesium, tin and lead and others should shift proportionately to the cube roots of their atomic weights, because the cube roots of their atomic weights are to each other, if the particles are of about the same density, as their linear dimensions. Or, on the other hand, if, as seems possible, the shifts of the lines are to each other as the linear dimensions of the particles themselves

they are, then, it follows that analogous elements — elements of the same half of a Mendeléeff group, differ from one another in the same manner because of the difference in the linear dimensions of their molecules.

Again I wish to say that these suggestions are offered with the greatest hesitation, and only with the hope that they may be of some service in suggesting out further investigations along this line of spectrum analysis.

History of the present Investigation.

Work was begun on this investigation in February 1895 by Mr. J. F. Mohler and myself, and continued as joint work till December of the same year. Our accumulated results on twenty-three elements were then published in the

December number of the Astrophysical Journal for 1895, and likewise, though in a less complete form, in the Johns Hopkins University Circular for February 1896. Some account of it had also been given by Mr. [illegible] at the Springfield 1895 meeting of the American Association for the Advancement of Science.

The article in the Astrophysical Journal, December, 1895, by Jewell, Mohler and [illegible] showed how the shifts of the lines could be used in roughly approximating the pressure of the reversing layer of the sun's atmosphere, and gave a few first approximations for several elements.

After the publications of these papers, Mr. Mohler examined alone the effect of very low pressures on a part of the spectrum and published his results in

the Astrophysical Journal of October, 1896. And, by working independently, examined the behavior of a number of additional elements and published the results in the Astrophysical Journal of November, 1896.

The present paper contains much that is new — the behavior of several additional elements (so that the metallic elements are now practically exhausted), the behavior of different groups of analogous lines like those of iron and copper, and in particular the different series of lines as furnished by lithium, sodium, zinc and [illegible], and also a further study of several of the elements, iron, zinc, copper, cadmium, in previous studies by [illegible] and myself.

Of the relations [illegible] the [illegible] [illegible] were noted by [illegible]

and roughly [illegible] numbers [illegible] and [illegible]
[illegible] by [illegible]. Number eight was also
[illegible] by [illegible] and at the suggestion [illegible]
and confirmed by Mohler. Number ten is also
entirely to Mohler, while numbers three,
seven, eleven, twelve and thirteen are my
own observations, as is also the present form
of number nine, though that merely differs
in [illegible] [illegible] [illegible] was previously
[illegible] to Mohler and my work on the
[illegible] of the [illegible] of [illegible].
The first use of [illegible] [illegible] of [illegible] of the
[illegible] [illegible] was made by [illegible]
[illegible] of the [illegible] of the H, K and
g lines of calcium.

Among the [illegible] [illegible] [illegible] [illegible]
[illegible] [illegible] [illegible] [illegible] [illegible] [illegible]
[illegible]. [illegible] [illegible] [illegible] [illegible] [illegible]
[illegible] [illegible] [illegible] many independent of

and at the same time most important are numbers one, two, three, six, seven eight and thirteen.

Description of Plate IV.

Some idea of the effect of pressure on spectral lines may be got from plate IV. which is a print from a few of the negatives obtained during the course of my work. I. shows the pair of sodium lines λ 3302.504 and λ 3303.119. The inner portion was taken at a pressure of eight and one half atmospheres and the outer portions at one atmosphere. On the whole the unsymmetrical widening of these lines is clearly seen, the spreading being to the violet, yet, as shown by the plate, the lines under pressure are greatly

shifted towards the end of the spectrum.
II is from the [illegible], the
inner portion being taken at a pressure of
twelve atmospheres. This shows several of the
iron lines, those marked, that shift to
a greater extent than the other lines.
It shows too a portion of a [illegible] that
those lines are not [illegible]
[illegible]
under pressure more readily than at
normal pressure. III, the inner portion
of which was formed at a pressure of
seven atmospheres, shows the great
difference in the shifts of the [illegible]
of copper lines. In this case the spark
was taken [illegible]
a copper and a brass rod, the brass
forming the [illegible] pole.
The chief points of interest about V.

on the [illegible] lines (in the cyanogen band) and the calcium line g. The shifts are very evident. The pressure in this case was eight and one half atmospheres. The outside as usual being at one atmosphere. The last plate, V. shows the pair of potassium lines λ4044.294 and λ4047.338, which are greatly shifted. The small line between them is due to iron. In this case the pressures were also eight and a half and one atmosphere, in fact V. is from a different portion of the same plate from which IV. was taken.

Acknowledgement.

While the labor of accumulating the results tabulated in this paper is, in the main, my own, the beginning and the continuation of the investigation and the lines along which it was pursued are all due in one way or another, to Professor Rowland and Dr. Ames directors of the Physical Laboratory; and I am glad of this opportunity to state my sincere appreciation not only for their assistance every time it was needed, but also for the thoroughly kind and helpful manner in which it was invariably given.

I wish also to thank Mr. L. E. Jewell for the willingness with which he often brought his extensive knowledge of the spectra of the elements to my aid.

Biographical Sketch.

The author was born in Monroe County, West Virginia, February 3, [illegible]. He graduated as Bachelor of Arts from the Washington and Lee University, Virginia, in 1886, and as Civil Engineer in 1888. He also graduated from the Schools of Chemistry and the School of Physics of the University of Virginia in 1889. From 1889 to 1893 he had charge of the departments of Physics and Mathematics in the Miller Manual Labor School of Albemarle, Virginia; and during the year 1893–1894 he had the chair of Physics and Chemistry in Washington College, Maryland.

Since the fall of 1894 he has pursued, at The Johns Hopkins University, graduate courses in Physics, Chemistry and Mathematics. He was awarded for 1894–1895 an Honorary Hopkins Scholarship (Virginia) and a Fellowship in Physics for 1895–1896. At present he is Fellow by Courtesy and Student Assistant in Physics.

Plate I.

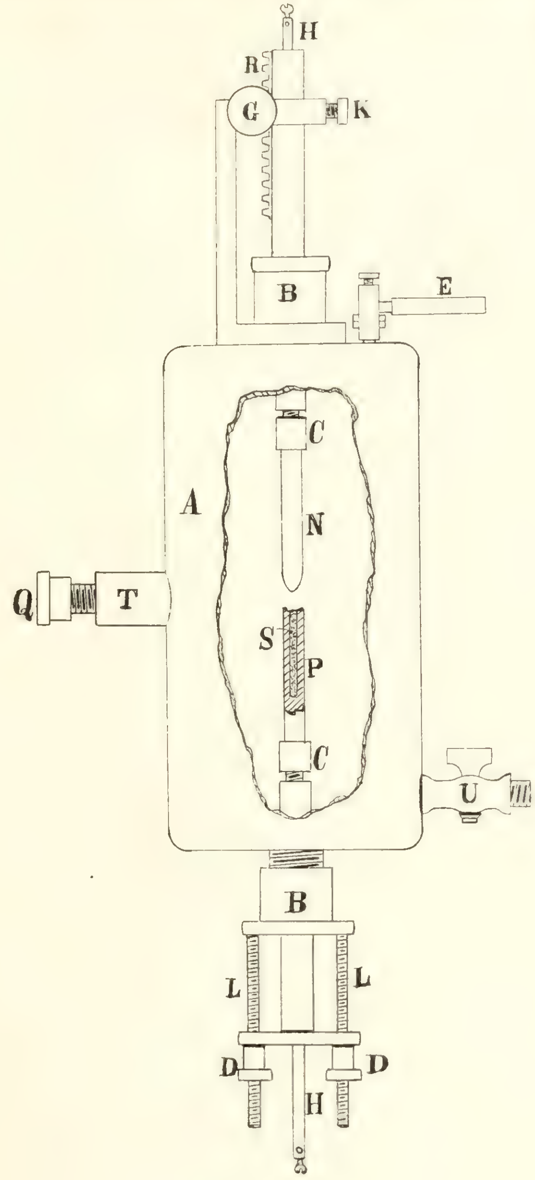


Plate II.

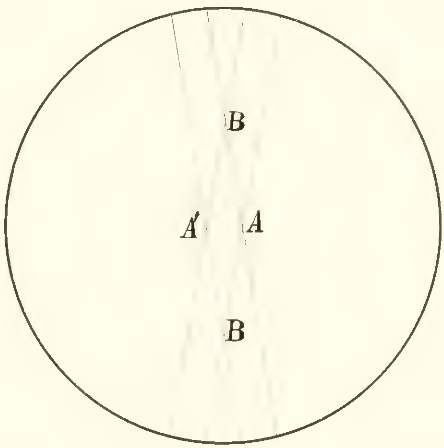
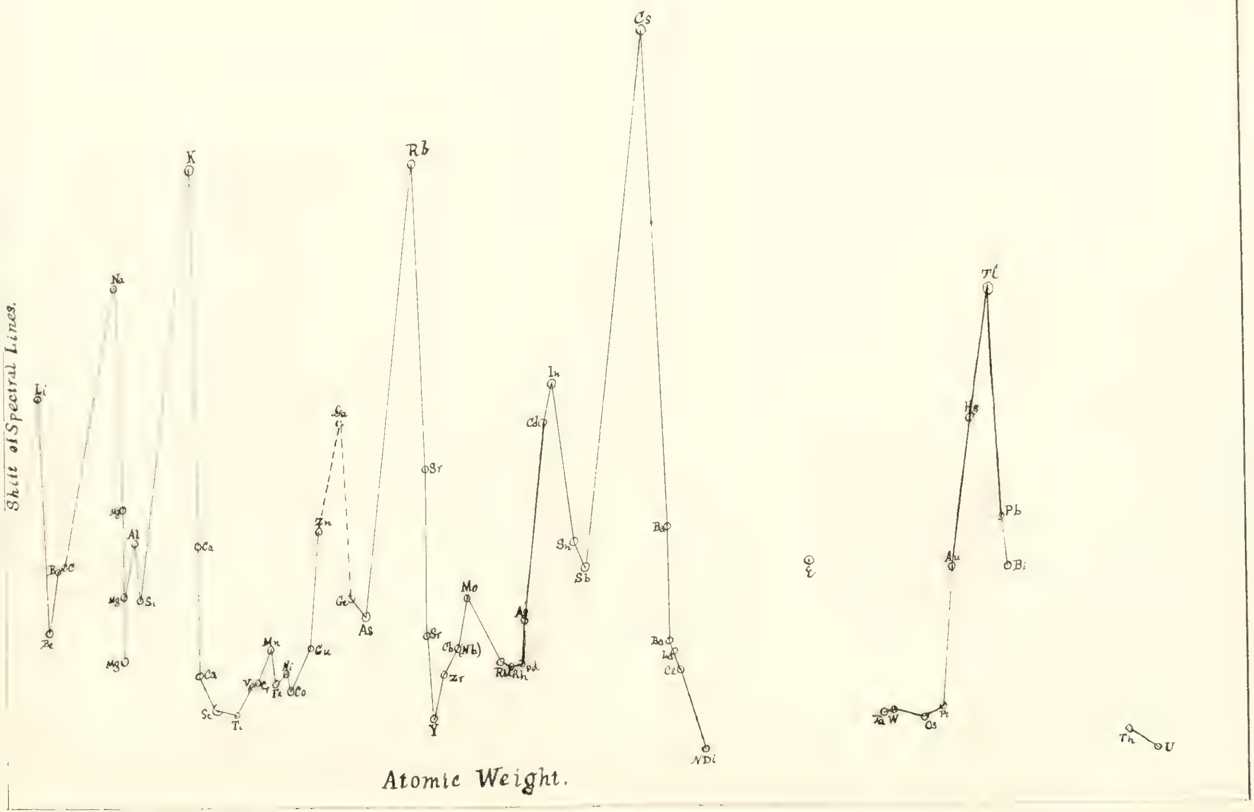
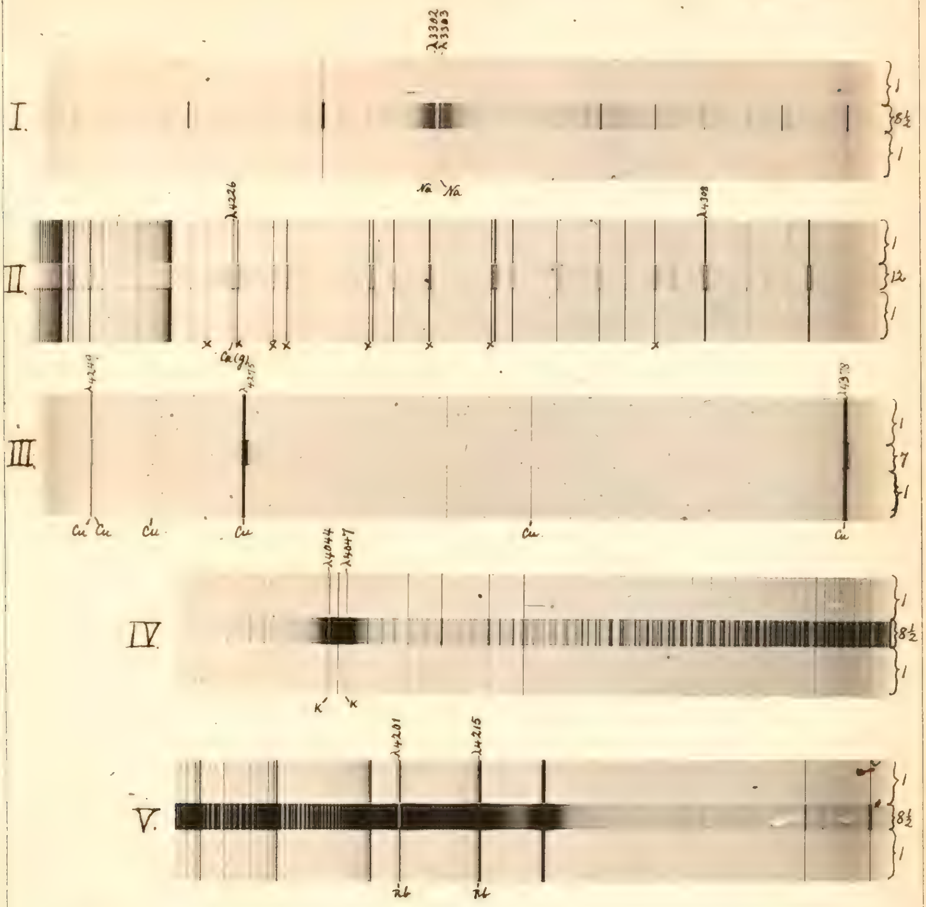


Plate III.



Shift of Spectral Lines.
Atomic Weight.
Li
Be
B
C
Na
Mg
Al
Si
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Ni
Co
Cu
Zn
Ga
Ge
As
Rb
Sr
Y
Zr
Cb(Nb)
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Cs
Ba
La
Ce
NDi
Ta
W
Os
Pt
Au
Hg
Tl
Pb
Bi
Th
U

Plate IV.



Copy of plates (exact size) showing shifts of lines. Sides in each case, at one atmosphere; middle at higher pressure.

I. Shows a pair of sodium lines that spread to the violet, but shift to the red.

II. Chiefly iron (from new Concord meteorite). Shows iron lines (x) of large shift, and carbon (Cy) band not shifted

III. Shows large shift of one class of copper lines, small shift of another. One pole was a copper rod, the other a brass rod

IV. Shows one pair of potassium lines.

V. Shows two rubidium lines.